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- Nishida, Hiroshi  
Ichihara-shi, Chiba (JP)
- Abekawa, Hiroaki  
Ichihara-shi, Chiba (JP)

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(74) Representative: Cresswell, Thomas Anthony  
J.A. KEMP & CO.  
14 South Square  
Gray's Inn  
London WC1R 5LX (GB)

(71) Applicant: SUMITOMO CHEMICAL COMPANY

LIMITED

Osaka-shi, Osaka 541 (JP)

(72) Inventors:

- Hibi, Takuo  
Ichihara-shi, Chiba (JP)

### (54) Process for producing chlorine

(57) The present invention provides a process for producing chlorine by oxidation of hydrogen chloride with oxygen which process comprises using a ruthenium catalyst.

EP 0 743 277 A1

## Description

The present invention relates to a process for producing chlorine. More particularly, it relates to a process for producing chlorine, comprising oxidation of hydrogen chloride, which makes it possible to produce chlorine at a lower reaction temperature using a smaller amount of catalyst having high activity.

It is known that chlorine is useful as a raw material of vinyl chloride, phosgene, etc., and can be produced by oxidation of hydrogen chloride. In Japanese Patent Kokai (Laid-Open) No. 62-270405, for example, a process for producing chlorine, comprising oxidation of hydrogen chloride using a chromium oxide catalyst is described. However, the process which has hitherto been known has a problem that an activity of the catalyst is insufficient, and there has been desired to develop a catalyst having high activity, which can be used for the oxidation reaction of hydrogen chloride.

When using a supported ruthenium catalyst for a general oxidation reaction with oxygen, ruthenium in the high oxidation state was sometimes volatilized at elevated temperature. Therefore, it has hitherto been considered that it is difficult to use the supported ruthenium catalyst for the said reaction. The present inventors have found first that the ruthenium catalyst shows high activity when using it for the reaction for producing chlorine by oxidation of hydrogen chloride, and have studied more intensively. Thus the present invention has been completed.

That is, a main object of the present invention is to provide a process for producing chlorine, comprising oxidation of hydrogen chloride, which makes it possible to produce chlorine at a lower reaction temperature using smaller amount of a catalyst having high activity.

This object as well as other objects and advantages of the present invention will become apparent to those skilled in the art from the following description.

That is, the present invention provides a process for producing chlorine by oxidation of hydrogen chloride with oxygen which process comprises using a ruthenium catalyst.

The ruthenium catalyst used for the present invention means a catalyst containing at least ruthenium or a ruthenium compound, and examples thereof include commercially available supported ruthenium catalyst, ruthenium oxide catalyst, catalyst obtained by supporting a ruthenium compound on a carrier, ruthenium mixed oxide catalyst, ruthenium black, etc.

Examples of the supported catalyst include supported metal ruthenium catalyst etc. which are prepared by supporting on a carrier such as alumina, silica, silica alumina, zeolite, diatomaceous earth, oxide and mixed oxide of elements (e.g. titanium oxide, zirconium oxide, vanadium oxide, etc.), metal sulfate, etc. according to a known process (see Shokubai Kouza, Shokubai Jikken Handbook, 1986, page 20, published by Kodan-sha). Commercially available catalysts can also be used. The carrier used for the supported catalyst is not specifically

limited, and there can be preferably used titanium oxide, alumina, zirconium oxide, zeolite, silica, titanium composite oxide, zirconium composite oxide and aluminum composite oxide, more preferably titanium oxide, zirconium oxide and alumina.

The content of ruthenium is preferably from 0.1 to 20% by weight based on the carrier, more preferably from 1 to 5% by weight based on the carrier. A third component other than ruthenium can also be added, and examples of the third component include palladium compound, copper compound, chromium compound, vanadium compound, alkali metal compound, rare earth compound, manganese compound, alkaline earth compound, etc. The amount of the third component added is usually from 0.1 to 10% by weight based on the carrier.

A supported ruthenium catalyst can be used after reduction of the catalyst or after oxidation of it.

Examples of the ruthenium oxide catalyst include ruthenium oxides such as ruthenium dioxide, ruthenium hydroxide etc., a ruthenium dioxide catalyst and ruthenium hydroxide catalyst etc. prepared according to a known method (see Gensobetsu Shokubai Binran, 1978, page 544, published by Chijinkan). Commercially available ruthenium dioxide can also be used. The ruthenium oxide compound such as halogenated ruthenium oxide, in which ruthenium and other elements are combined, may also be used.

As the preparation method of ruthenium dioxide, for example, there is a method comprising adding an alkali to an aqueous solution of  $\text{RuCl}_3$ , precipitating ruthenium hydroxide, washing the precipitate, followed by calcining in air.

A catalyst obtained by supporting a ruthenium oxide compound on a carrier is preferably used. Examples of the carrier include oxide and mixed oxide of elements (e.g. titanium oxide, alumina, zirconium oxide, silica, titanium mixed oxide, zirconium mixed oxide, aluminum mixed oxide, silicon mixed oxide etc.) The weight ratio of the ruthenium oxide compound to the carrier is usually 0.1/99.9 to 70/30. Examples of the supported ruthenium oxide compounds include ruthenium oxide, ruthenium hydroxide, halogenated ruthenium oxide. As the supporting method of ruthenium oxide, for example, there is a method comprising impregnating the carrier with an aqueous solution of  $\text{RuCl}_3$ , adding an alkali, precipitating ruthenium hydroxide on the carrier, washing it with water, followed by calcining in air. As another example, there is a method comprising impregnating the carrier with an aqueous solution of  $\text{RuCl}_3$ , drying, followed by oxidative decomposition under calcination in air. The supported catalyst is usually calcined at 100°C to 500°C for about 30 minutes to 5 hours.

Examples of the catalyst prepared by supporting the ruthenium compound on the carrier include catalysts prepared by supporting compounds such as ruthenium chloride (e.g.  $\text{RuCl}_3$ ,  $\text{RuCl}_3$  hydrate, etc.), salt of chlororuthenate (e.g.  $\text{K}_3\text{RuCl}_6$ ,  $[\text{RuCl}_6]^{3-}$ ,  $\text{K}_2\text{RuCl}_6$ , etc.), salt of chlororuthenate hydrate (e.g.  $[\text{RuCl}_5(\text{H}_2\text{O})]^2-$ ,  $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ , etc.), ruthenium oxide

(e.g. RuO<sub>2</sub>, RuO<sub>4</sub>, etc.), salt of ruthenic acid (e.g. K<sub>2</sub>RuO<sub>4</sub>, etc.), ruthenium oxychloride (e.g. Ru<sub>2</sub>OCl<sub>4</sub>, Ru<sub>2</sub>OCl<sub>5</sub>, Ru<sub>2</sub>OCl<sub>6</sub>, etc.), salt of ruthenium oxychloride (e.g. K<sub>2</sub>Ru<sub>2</sub>OCl<sub>10</sub>, Cs<sub>2</sub>RuO<sub>2</sub>Cl<sub>4</sub>, etc.), ruthenium hydroxide, ruthenium-amine complex (e.g. [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, [Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]<sup>2+</sup>, etc.), chloride of ruthenium-amine complex (e.g. [Ru(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup>, [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>, [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>, etc.), ruthenium bromide (e.g. RuBr<sub>3</sub>, RuBr<sub>3</sub> hydrate, etc.), other ruthenium-organic amine complex, ruthenium-acetyl acetone complex, ruthenium-carbonyl complex (e.g. Ru(CO)<sub>5</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, etc.), salt of ruthenium organic acid (e.g. Ru<sub>2</sub>(RCOO)<sub>4</sub>Cl (R = alkyl group), etc.), ruthenium-nitrosyl complex, ruthenium-phosphine complex, etc. on carriers such as alumina, silica, silica alumina, zeolite, diatomaceous earth, oxide and mixed oxide of elements (e.g. titanium oxide, zirconium oxide, vanadium oxide, etc.), metal sulfate, etc. Two or more sorts of these carriers may be used in combination. As the ruthenium compound, ruthenium chloride, ruthenium chloride-amine complex and ruthenium-carbonyl complex are preferred. As the carrier, titanium oxide, zirconium oxide, alumina, silica, titanium mixed oxide, zirconium mixed oxide and aluminum mixed oxide are preferably used. Among them, titanium oxide, alumina, zirconium oxide and silica are particularly preferred.

Additional examples of the catalyst include catalyst obtained by calcining the above catalyst, followed by combining with the carrier, catalyst subjected to a reducing treatment and catalyst subjected to an oxidizing treatment.

The content of the ruthenium compound is usually from 0.1 to 20% by weight based on the carrier, preferably from 1 to 10% by weight based on the carrier. A third component other than the ruthenium compound can also be added, and examples of the third component include palladium compound, copper compound, chromium compound, vanadium compound, alkali metal compound, rare earth compound, manganese compound, alkaline earth compound, etc. The amount of the third component added is usually from 0.1 to 10% by weight based on the carrier. Examples of the supporting process include impregnation process, precipitation supporting process, coprecipitation process, mixing process, etc. Among them, the impregnation process is preferred.

As the impregnation process, for example, there is a process comprising suspending a carrier in a solution, which is prepared by dissolving a ruthenium compound in a solvent, evaporating the solvent, followed by drying and further calcining. Examples of the solvent include water, methanol, organic solvent, etc.

The supported catalyst is usually calcined at 100 to 500°C for about 30 minutes to 5 hours.

The catalyst according to the method for preparing the ruthenium mixed oxide is obtained by chemically-mixing or complexing at least one oxide selected from oxides such as titanium oxide, zirconium oxide, alumina, silica, vanadium oxide, boron oxide, chromium oxide,

nobium oxide, hafnium oxide, tantalum oxide, tungsten oxide, etc. with ruthenium oxide. The compound for chemically-mixing with ruthenium oxide is not limited to the above compounds, and various mixed oxides such as copper chromite, etc. are also used. As the process for chemically-mixing ruthenium, for example, there is a process comprising adding a hydrolyzate of the ruthenium compound (e.g. ruthenium chloride, etc.) to a hydrolyzate of chloride, oxychloride, nitrate, oxynitrate, 5 alkaline salt of oxy-acid, sulfate, alkoxide, etc. of titanium etc., filtering and washing the mixture, followed by calcining in air. Examples of the ruthenium compound include compounds described as examples of the catalyst obtained by supporting the ruthenium compound (e.g. ruthenium chloride, etc.) with the carrier. RuCl<sub>3</sub> and RuCl<sub>3</sub> hydrate are preferred. Preferred examples of the oxide for chemically-mixing with ruthenium oxide include titanium oxide, zirconium oxide, alumina, silica, titanium mixed oxide, zirconium mixed oxide, aluminum mixed oxide and silicon mixed oxide. As the process for supporting the ruthenium mixed oxide with the carrier, for example, there is a process comprising impregnating the carrier with chloride, nitrate, etc. of titanium and the ruthenium compound such as ruthenium chloride, followed by calcining in air. Examples of the carrier include 10 titanium oxide, alumina, silica, zirconium oxide or a mixed oxide thereof. The amount of the ruthenium oxide contained in the ruthenium mixed oxide is usually from 0.1 to 80% by weight, preferably from 1 to 70% by weight. A third component can also be added, and examples of the third component include palladium compound, copper compound, chromium compound, vanadium compound, alkali metal compound, rare earth compound, manganese compound, alkaline earth compound, etc. The amount of the third component added is 15 usually from 0.1 to 10% by weight based on the weight of the ruthenium mixed oxide.

Examples of the process for preparing the ruthenium mixed oxide include coprecipitation process, process due to mixing of precipitate, impregnation process, etc. The ruthenium mixed oxide is usually prepared by calcining at 200 to 1000°C for about 1 to 5 hours. It is preferably calcined at 300°C to 500°C.

Examples of the process for supporting the ruthenium mixed oxide on the carrier include impregnation process, precipitation supporting process, etc. The supported catalyst is usually calcined at 200°C to 1000°C for about 1 to 5 hours. It is preferably calcined at 300°C to 500°C. Examples of the calcining atmosphere include nitrogen, air, etc..

Examples of the catalyst other than the above catalysts include ruthenium black prepared by a known process (see "Shokubai Chousei Kagaku", 1980, page 233, published by Kodan-sha) and a supported catalyst containing ruthenium in an amount of more than 20% by weight based on the carrier.

According to the present invention, chlorine is produced by oxidation of hydrogen chloride with oxygen using a ruthenium catalyst. The reaction system in the

production of chlorine is not specifically limited, but a flow system is preferred and a fixed bed gas phase flow system is more preferred. When the reaction temperature is high, the ruthenium oxide in the high oxidation state is sometimes volatilized and, therefore, the reaction is preferably conducted at lower temperature, more preferably from 100°C to 500°C, most preferably from 200°C to 380°C. Also, the reaction pressure is not specifically limited, but is preferably from about atmospheric pressure to 50 atm. As the oxygen raw material, air may be used as it is or air enriched in oxygen or pure oxygen may be used. Since other components are discharged simultaneously when an inherent nitrogen gas is discharged from the apparatus, pure oxygen containing no inherent gas is preferred. A theoretical molar amount of 0.25 mol of oxygen per mol of hydrogen chloride is required for oxidation to chlorine, but oxygen is preferably supplied in a 0.1-fold to 10-fold amount, more preferably in a 0.2-fold to 5-fold amount, compared with the theoretical amount.

When the flow rate of the raw material, hydrogen chloride, to the catalyst is represented by gas hourly space velocity (GHSV) under atmospheric pressure in the case of the fixed bed gas phase flow system, GHSV is preferably from about 10 h<sup>-1</sup> to 20000 h<sup>-1</sup>, more preferably from about 20 h<sup>-1</sup> to 1000 h<sup>-1</sup>. The GHSV is equal to the supplying rate of hydrogen chloride divided by the (packed) volume of solid catalyst.

It becomes possible to produce chlorine at low temperature, which is advantageous in view of equilibrium, by using the ruthenium catalyst having high activity. It also become possible to inhibit loss of an active component in the reaction due to volatilization of ruthenium, which has hitherto been considered to be a problem in the supported ruthenium catalyst, ruthenium oxide catalyst, catalyst obtained by supporting the ruthenium compound on the carrier, catalyst obtained by the process for preparing the ruthenium mixed oxide, and ruthenium black.

The following Examples and Comparative Examples further illustrate the present invention in detail.

#### Example 1

A catalyst was prepared by the following process. That is, water (8.6 g) was charged in an ice-cooled flask, and commercially available titanium tetrachloride (7.6 g) was added dropwise with stirring to prepare an aqueous titanium tetrachloride solution. Then, a solution prepared by dissolving commercially available zirconium oxychloride octahydrate (13.1 g) in water (43.3 g) was added dropwise to the aqueous titanium tetrachloride solution with stirring to prepare a homogeneous solution. A solution prepared by adding 36 % hydrochloric acid (1.1 g) to a solution of ammonium sulfate (13.4 g) and water (26.8 g) was poured into the above homogeneous solution, followed by stirring to prepare an homogeneous solution. Then, the homogeneous solution was heated to 70°C and an aqueous 25 wt % ammonia solu-

tion (30.3 g) was slowly added dropwise with stirring. As the solution was added dropwise, a white precipitate was formed. After adding dropwise, the mixture was stirred at the same temperature for one hour. After stirring, the precipitate was filtered, washed with distilled water (300 ml) and then filtered again. After this operation was repeated three times, the resultant was suspended in water (150 ml). Then, a solution prepared by dissolving commercially available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) (9.74 g) in water (60 g) and a solution prepared by dissolving sodium hydroxide (5.2 g, content: 96 %) in water (20 g) were mixed and stirred, after stirring, the mixed solution was immediately added dropwise to the suspension with stirring. Water (40 ml) was further added. After adding, a solution prepared by diluting 61 wt % nitric acid (2.2 g) with water (30 g) was added dropwise, followed by stirring at room temperature for one hour. After stirring, the black precipitate was filtered. The precipitate was washed with distilled water (300 ml) and then filtered again. After this operation was repeated three times, the resultant was dried at 60°C for 4 hours to obtain 16.3 g of a black solid. This solid was ground, heated in air from room temperature to 350°C over 3.5 hours and then calcined at the same temperature for 3 hours to obtain 13.5 g of a black catalyst. According to the same manner as that described above, 55.4 g of the same catalyst was obtained. The calculated value of the content of the ruthenium oxide was 36 % by weight. The resulting powder was granulated to obtain a ruthenium oxide-titanium oxide-zirconium oxide catalyst of 12 to 18.5 mesh.

The ruthenium oxide-titanium oxide-zirconium oxide catalyst (46.8 g) thus obtained was charged in a quartz glass reaction tube (inner diameter: 22 mm). A hydrogen chloride gas (19.0 ml/min.) and an oxygen gas (9.3 ml/min.) were respectively supplied under atmospheric pressure (converted on the basis of 0°C, 1 atm). The quartz glass reaction tube was heated with an electric furnace to adjust the inner temperature (hot spot) to 265°C. Six hours after the beginning of the reaction, the gas at the reaction outlet was sampled by passing it through an aqueous 30 % potassium iodide solution, and then the amount of chlorine formed and amount of the non-reacted hydrogen chloride were respectively determined by iodometric titration and neutralization titration process. As a result, the conversion of hydrogen chloride was 95.9%.

#### Example 2

The ruthenium oxide-titanium oxide-zirconium oxide catalyst which is the same as that used in Example 1 (2.5 g) was diluted by mixing sufficiently with a titanium oxide catalyst of 12 to 18.5 mesh (5 g), followed by charging in a quartz glass reaction tube (inner diameter: 12mm). A hydrogen chloride gas (200 ml/min.) and an oxygen gas (200 ml/min.) were respectively supplied under atmospheric pressure (converted on the basis of 0°C, 1 atm). The quartz glass reaction tube was heated

with an electric furnace to adjust the inner temperature (hot spot) to 301°C. 2.9 Hours after the beginning of the reaction, the gas at the reaction outlet was sampled by passing it through an aqueous 30 % potassium iodide solution, and then the amount of chlorine formed and amount of the non-reacted hydrogen chloride were respectively determined by iodometric titration and neutralization titration processes. The catalyst activity of chlorine formation per unit weight of the catalyst determined by the following equation was  $7.35 \times 10^{-4}$  mol/min g catalyst. The catalyst activity of chlorine formation per unit weight of catalyst (mol/min g catalyst) = amount of outlet chlorine formed (mol/min)/weight of catalyst (g)

#### Example 3

A catalyst was prepared by the following process. That is, water (27.0 g) was charged in an ice-cooled flask, and commercially available titanium tetrachloride (14.3 g) was added dropwise with stirring to prepare an aqueous titanium tetrachloride solution. Water (1222 g) was added to the solution at room temperature, and then a solution of urea (27.6 g) and water (100 g) was poured into the solution, followed by stirring to prepare an homogeneous solution. Then, the homogeneous solution was stirred with heating to 100°C for 2 hours. A white precipitate was formed gradually. Then, a solution of urea (3.2 g) and water (26 g) was added at the same temperature and, after stirring sufficiently, the precipitate was filtered. The precipitate was washed with distilled water (300 ml) and then filtered again. After this operation was repeated three times, the resultant was suspended in water (150 ml). Then, a solution prepared by dissolving commercially available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) (7.12 g) in water (54 g) and a solution prepared by dissolving sodium hydroxide (3.8 g, content: 96 %) in water (20 g) were mixed and stirred, after stirring, the mixed solution was immediately added dropwise to the suspension with stirring. After adding dropwise, a solution prepared by diluting 61 wt % nitric acid (1.57 g) with water (24 g) was added dropwise, followed by stirring at room temperature for one hour. After stirring, the black precipitate was filtered. The precipitate was washed with distilled water (300 ml) and then filtered again. After this operation was repeated three times, the resultant was dried at 60°C for 4 hours to obtain 9.3 g of a black solid. This solid was ground, heated in air from room temperature to 350°C over 3.5 hours and then calcined at the same temperature for 3 hours to obtain 8.1 g of a black catalyst. The calculated value of the content of the ruthenium oxide was 36 % by weight. The resulting powder was granulated to obtain a ruthenium oxide-titanium oxide catalyst of 12 to 18.5 mesh.

According to the same reaction manner as that described in Example 2 except for charging the obtained ruthenium oxide-titanium oxide catalyst (1.9 g) in a quartz glass reaction tube and adjusting the inner temperature to 300°C, the reaction was carried out. The

catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 1.9 hours had passed since the beginning of the reaction was  $9.05 \times 10^{-4}$  mol/min g catalyst.

#### Example 4

A catalyst was prepared by the following process. That is, an aqueous 20 wt % (as  $\text{TiOSO}_4$ ) titanium sulfate solution (54.7 g, manufactured by Wako Junyaku Kogyo Co., Ltd.) was diluted with water (110.3 g). The resulting solution was charged in an ice-cooled flask, and an aqueous 25 wt % ammonia solution (48.2 g) was added dropwise with stirring. As a result, a white precipitate was formed gradually. After stirring at room temperature for 30 minutes, the precipitate was filtered. The precipitate was washed with distilled water (300 ml) and then filtered again. After this operation was repeated three times, the resultant was suspended in water (150 ml). Then, a solution prepared by dissolving commercially available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) (9.86 g) in water (61 g) and a solution prepared by dissolving sodium hydroxide (5.2 g, content: 96 %) in water (20 g) were mixed and stirred, after stirring, the mixed solution was immediately added dropwise to the suspension with stirring. After adding dropwise, a solution prepared by diluting 61 wt % nitric acid (2.15 g) with water (30 g) was added dropwise, followed by stirring at room temperature for one hour. After stirring, the black precipitate was filtered, washed with distilled water (300 ml) and then filtered again. After this operation was repeated three times, the resultant was dried at 60°C for 4 hours to obtain 12.0 g of a black-solid. This solid was ground, heated in air from room temperature to 350°C over 3.5 hours and then calcined at the same temperature for 3 hours to obtain 9.9 g of a black catalyst. The calculated value of the content of the ruthenium oxide was 46 % by weight. The resulting powder was granulated to obtain a ruthenium oxide-titanium oxide catalyst of 12 to 18.5 mesh.

According to the same manner as that described in Example 2 except for charging the obtained ruthenium oxide-titanium oxide catalyst (2.5 g) in a reaction tube and adjusting the inner temperature to 299°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 2.6 hours had passed since the beginning of the reaction was  $7.35 \times 10^{-4}$  mol/min g catalyst.

#### Example 5

A catalyst was prepared by the following method. That is, commercially available titanium tetrabutoxide (15.4 g) was dissolved in ethanol (52 ml). Then, a solution prepared by dissolving commercially available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) (10.1 g) in water (122 ml) and a solution prepared by dissolving sodium hydroxide (14.8 g, content 96%) in water (60 ml) were mixed and stirred, after stirring, the mixed solution was

immediately added dropwise to the ethanol solution of titanium tetrabutoxide with stirring. As the solution was added dropwise, a precipitate was formed. After adding, the black suspension was stirred at room temperature sufficiently. Then, a solution prepared by diluting 61 wt% nitric acid (25.7 g) with water (62 g) was added dropwise, followed by stirring at room temperature for one hour. After stirring, the black precipitate was filtered. Then, the black precipitate was washed with distilled water (300 ml) and then filtered again. After this operation was repeated three times, the resultant was dried at 60 °C for 4 hours to obtain 10.5 g of a black solid. This solid was ground, heated in the air from room temperature to 350 °C over 3.5 hours and then calcined at the same temperature for 3 hours to obtain 8.4 g of a black catalyst. The calculated value of the content of the ruthenium oxide was 57 % by weight. The resulting powder was granulated to obtain a ruthenium oxide-titanium oxide catalyst of 12 to 18.5 mesh.

According to the same reaction manner as that described in Example 2 except for charging the obtained ruthenium oxide-titanium oxide catalyst (2.5 g) in a quartz glass reaction tube and adjusting the inner temperature to 300 °C, the reaction was carried out. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 1.9 hours had passed since the beginning of the reaction was  $7.7 \times 10^{-4}$  mol/min. g-catalyst.

#### Example 6

Commercially available ruthenium oxide hydrate ( $\text{RuO}_2$ , manufactured by Aldrich Chemical Co.) was granulated to obtain a ruthenium oxide catalyst of 12 to 18.5 mesh.

According to the same manner as that described in Example 2 except for charging the obtained ruthenium oxide catalyst (2.5 g) in a reaction tube and adjusting the inner temperature to 300 °C, the reaction was carried out. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 1.5 hours had passed since the beginning of the reaction was  $5.35 \times 10^{-4}$  mol/min. g-catalyst.

#### Example 7

A 2 wt % spherical ruthenium-titanium oxide catalyst having a particle size of 3mm diameter (manufactured by N.E. Chemcat Co.) was ground to adjust the particle size to 12 to 18.5 mesh. According to the same manner as that described in Example 2 except for charging this ruthenium-titanium oxide catalyst (2.5 g) in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (190 ml/min.) and adjusting the inner temperature to 300°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 1.5 hours had passed since the beginning of the reaction was  $1.38 \times 10^{-4}$  mol/min g catalyst.

#### Example 8

The 2 wt % ruthenium-titanium oxide catalyst which is the same as that used in Example 7 was ground to adjust the particle size to 12 to 18.5 mesh. According to the same manner as that described in Example 2 except for charging the catalyst (2.5 g) in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (196 ml/min.) and an oxygen gas (170 ml/min.) and adjusting the inner temperature to 380°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 2 hours had passed since the beginning of the reaction was  $11.4 \times 10^{-4}$  mol/min g catalyst.

#### Example 9

A 2 wt % ruthenium-zirconium oxide catalyst (1/8 inch pellet, manufactured by N.E. Chemcat Co.) was ground to adjust the particle size to 12 to 18.5 mesh. According to the same manner as that described in Example 2 except for charging this ruthenium-zirconium oxide catalyst (2.5 g) in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (196 ml/min.) and an oxygen gas (170 ml/min.) and adjusting the inner temperature to 380°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 3 hours had passed since the beginning of the reaction was  $7.9 \times 10^{-4}$  mol/min g catalyst. The residual hydrogen chloride flow was  $4.7 \times 10^{-3}$  mol/min.

#### Example 10

A 5 wt % ruthenium-alumina powder catalyst (manufactured by N.E. Chemcat Co.) was granulated to obtain a catalyst of 12 to 18.5 mesh. According to the same manner as that described in Example 2 except for charging this granulated ruthenium-aluminum catalyst (2.5 g) in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (193 ml/min.) and adjusting the inner temperature to 380°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 10 hours had passed since the beginning of the reaction was  $6.7 \times 10^{-4}$  mol/min g catalyst.

#### Example 11

A catalyst was prepared by the following process. That is, silica AEROSIL 300 (18.70 g, manufactured by Nihon Aerosil Co., Ltd.) was suspended in an aqueous solution of commercially available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , 1.02 g) and water (80 g), and then the mixture was evaporated to dryness at 55 to 60°C using a rotary evaporator and heated in a nitrogen flow at 150°C for one hour to obtain 18.1 g of a green-black ruthenium chloride catalyst. The ratio of  $\text{RuCl}_3$  to

the carrier was 5 % by weight. This catalyst was granulated to obtain a catalyst of 12 to 18.5 mesh.

According to the same manner as that described in Example 2 except for charging the resulting ruthenium chloride catalyst (5 g) in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (194 ml/min.) and adjusting the inner temperature to 380°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 5 hours had passed since the beginning of the reaction was  $5.9 \times 10^{-4}$  mol/min g catalyst.

#### Comparative Example 1

A catalyst was prepared by the following process. That is, chromium nitrate enneahydrate (60.3 g) was dissolved in water (600 ml) and the solution was heated to 45°C. Then, 25 wt % ammonia water (64.9 g) was added dropwise over 1.5 hours with stirring, followed by stirring at the same temperature for additional 30 minutes. Water (3.3 liter) was added to the formed precipitate and, after standing overnight to cause sedimentation, the supernatant was removed by decantation. Then, water (2.7 liter) was added, followed by stirring sufficiently for 30 minutes. After the precipitate was washed by repeating this operation five times, the supernatant was removed by decantation. Then, 20 wt % silica sol (49 g) was added and, after stirring, the mixture was evaporated to dryness at 60°C using a rotary evaporator. The resultant was dried at 60°C for 8 hours and then dried at 120°C for 6 hours to obtain a green solid. This solid was dried in a nitrogen flow at 120°C for 6 hours and then cooled to room temperature to obtain a green solid. Then, this solid was calcined at 600 °C for 3 hours in the air and granulated to obtain a Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst of 12 to 18.5 mesh.

According to the same manner as that described in Example 2 except for charging the resulting Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst (2.5 g) in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (192 ml/min.) and adjusting the inner temperature to 301 °C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 3.7 hours had passed since the beginning of the reaction was  $0.19 \times 10^{-4}$  mol/min g catalyst.

#### Comparative Example 2

According to the same manner as that described in Example 2 except for charging the Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst (2.5 g) used in Comparative Example 1 in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (192 ml/min.) and adjusting the inner temperature to 380°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which

5.8 hours had passed since the beginning of the reaction was  $2.1 \times 10^{-4}$  mol/min g catalyst.

#### Comparative Example 3

According to the same manner as that described in Example 2 except for charging the Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst (5 g) used in Comparative Example 1 in a reaction tube without diluting with a titanium oxide carrier, supplying a hydrogen chloride gas (96.5 ml/min.) and adjusting the inner temperature to 380°C, the reaction was conducted. The catalyst activity of chlorine formation per unit weight of the catalyst at the time at which 5 hours had passed since the beginning of the reaction was  $2.7 \times 10^{-4}$  mol/min g catalyst.

#### Claims

1. A process for producing chlorine by oxidation of hydrogen chloride with oxygen which process comprises using a ruthenium catalyst.
2. A process according to claim 1, wherein the ruthenium catalyst is a supported metal ruthenium catalyst which is obtainable by supporting ruthenium on a carrier.
3. A process according to claim 1, wherein the ruthenium catalyst is a ruthenium oxide catalyst.
4. A process according to claim 1, wherein the ruthenium catalyst is a catalyst obtainable by supporting a ruthenium compound on a carrier.
5. A process according to claim 1, wherein the ruthenium catalyst is a catalyst obtainable by a process for preparing a ruthenium mixed oxide.
6. A process according to claim 2, wherein the carrier is at least one carrier selected from titanium oxide, alumina, zirconium oxide, zeolite, silica, titanium mixed oxide, zirconium mixed oxide and aluminum mixed oxide.
7. A process according to claim 2 or 6, wherein the content of ruthenium to the carrier is from 0.1 to 20% by weight.
8. A process according to claim 3, wherein the ruthenium oxide catalyst is a ruthenium oxide and/or ruthenium hydroxide.
9. A process according to claim 3 or 8, wherein the ruthenium oxide catalyst is a supported ruthenium oxide catalyst.
10. A process according to claim 9, wherein the carrier is at least one carrier selected from titanium oxide, alumina, zirconium oxide, silica, titanium mixed

oxide, zirconium mixed oxide, aluminum mixed oxide and silicon mixed oxide.

11. A process according to claim 9 or 10, wherein the ratio of ruthenium oxide to the carrier is from 5 0.1/99.9 to 70/30 by weight.

12. A process according to claim 4, wherein the ruthenium compound is at least one compound selected from ruthenium chloride, ruthenium chloride-amine 10 complex and ruthenium-carbonyl complex.

13. A process according to claim 4 or 12, wherein the carrier is at least one carrier selected from the group consisting of titanium oxide, alumina, zirconium oxide, silica, titanium mixed oxide, zirconium mixed oxide and aluminum mixed oxide. 15

14. A process according to any one of claims 4, 12 or 13, wherein the ratio of the ruthenium compound to the carrier is from 0.1 to 20% by weight. 20

15. A process according to claim 5, wherein the catalyst obtainable by a process for preparing a ruthenium mixed oxide comprises at least one oxide selected from titanium oxide, zirconium oxide, alumina, silica, titanium mixed oxide, zirconium mixed oxide, aluminum mixed oxide and silicon mixed oxide, in addition to ruthenium oxide. 25

16. A process according to claim 5 or 15, wherein the catalyst obtainable by a process for preparing a ruthenium mixed oxide comprises ruthenium oxide in an amount of 1 to 70% by weight. 30

17. Use of a ruthenium catalyst in the oxidation of hydrogen chloride with oxygen to produce chlorine. 35

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European Patent  
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## EUROPEAN SEARCH REPORT

Application Number  
EP 96 30 3526

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	DE-B-15 67 788 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 27 May 1970 * column 1, line 52 - column 2, line 10 *	1, 4, 12, 13, 17	C01B7/04
A, D	PATENT ABSTRACTS OF JAPAN vol. 012, no. 155 (C-494), 12 May 1988 & JP-A-62 270405 (MITSUI TOATSU CHEM INC), 24 November 1987, * abstract *	1	
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A	WO-A-91 06505 (UNIV SOUTHERN CALIFORNIA) 16 May 1991 * claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.)  C01B
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
BERLIN	19 July 1996	Clement, J-P	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
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